

Microplastic Abundance and Composition in Western Lake Superior As Determined via Microscopy, Pyr-GC/MS, and FTIR

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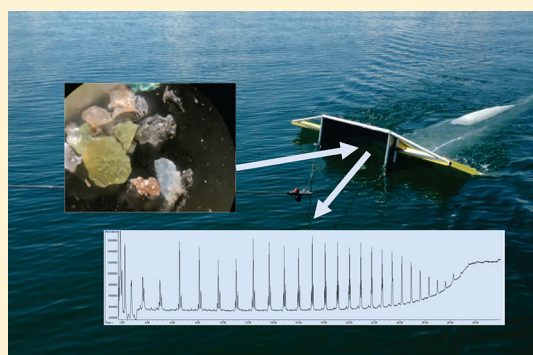
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S Supporting Information

ABSTRACT: While plastic pollution in marine and freshwater systems is an active area of research, there is not yet an in-depth understanding of the distributions, chemical compositions, and fates of plastics in aquatic environments. In this study, the magnitude, distribution, and common polymers of microplastic pollution in surface waters in western Lake Superior are determined. Analytical methodology, including estimates of ambient contamination during sample collection and processing, are described and employed. Microscopy, pyrolysis-gas chromatography/mass spectrometry (Pyr-GC/MS), and Fourier transform infrared spectroscopy (FTIR) were used to quantify and identify microplastic particles. In surface waters, fibers were the most frequently observed morphology, and, based upon PyGC/MS analysis, polyvinyl chloride was the most frequently observed polymer, followed by polypropylene and polyethylene. The most common polymer identified by FTIR was polyethylene. Despite the low human population in Lake Superior's watershed, microplastic particles (particularly fibers, fragments, and films) were identified in western-lake surface waters at levels comparable to average values reported in studies within Lake Michigan, the North Atlantic Ocean, and the South Pacific Ocean. This study provides insight into the magnitude of microplastic pollution in western Lake Superior, and describes in detail methodology to improve future microplastics studies in aquatic systems.



INTRODUCTION

Since the advent of mass-produced plastic in the middle of the 20th century, plastic pollution has become a significant environmental concern and a focus of recent study and remediation efforts in aquatic systems. Input vectors of plastic pollution to aquatic systems include wastewater treatment plants, shoreline debris, river outflows, landfills, industrial pollution, illegal dumping into aquatic systems, and atmospheric deposition.^{1–4}

Most plastic particles in oceanic gyres are less than 10 mm in length,^{5,6} which encompasses part of the mesoplastic size range as well as microplastic size range.⁴ Historically, “microplastic” particles have been inconsistently defined in terms of size.⁷ The definition established for the this study, defined by the National Oceanographic and Atmospheric Administration (NOAA), is a particle greater than 333 μm (as set by the plankton net used for collection) with no dimension longer than 5.0 mm.^{8,9} Microplastic particles have several recognized morphologies, including beads, foams, films, fragments, fibers, and other shapes resulting from the degradation of larger plastics.^{1,4,10,11}

Negative or potentially negative effects of microplastic pollution can include physical damage to organisms upon ingestion, false satiation, toxicological effects from adsorbed

substances, speculated toxicity from polymers and additives, and providing a vector for invasive species.^{11–13} Much of the focus on potential toxicological damage from microplastic pollution regards hydrophobic substances adsorbing to microplastic particles, including PCBs (polychlorinated biphenyls), DDT (dichlorodiphenyltrichloroethane) related compounds, and PAHs (polyaromatic hydrocarbons),¹² although the potential amount of uptake of these adsorbed substances from hydrophobic microplastic surfaces into organism biomass is not well-known. Recent research has revealed the presence of inorganic contaminants in microplastic paint pigments as well, including copper (Cu), lead (Pb), and cadmium (Cd),¹⁴ and the uptake of these pigment-related inorganic contaminants into aquatic organisms is unknown.

Much of the research regarding microplastic pollution has focused on marine systems with less research in freshwater systems.^{11,12} Recently, however, there has been an increasing interest in studying microplastics in freshwater systems,

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including investigations of lakes in Italy, Switzerland, Mongolia, East Africa, Canada, and the United States.^{15–24} Previous studies in the Laurentian Great Lakes have shown that microplastic pollution has a propensity to be elevated in surface waters in nearshore areas, especially near areas of high human population density and industrial activity, where extensive cleanup projects have not been performed.^{1,18,25} These studies have found that average open-water plastic densities resembled those in severely polluted ocean gyres^{1,18} and plastic was often found to be greater than 80% of anthropogenic shoreline debris items.¹ As with surface water studies, investigations of microplastics in benthic settings have typically been in marine environments,²³ although a study on Lake Ontario sediments, as well as sediments from affiliated tributaries and beaches, was conducted in 2016, revealing elevated concentrations in sediments near or in Humber Bay and Toronto Harbor.²⁴

Despite Lake Superior's status as the largest freshwater lake on earth by area, there is a lack of data, quantitatively and qualitatively, regarding microplastic pollution in this Laurentian Great Lake. Existing published data is from single measurements at five stations in the relatively unpopulated eastern basin of Superior and two tributaries flowing into the lake.^{18,26}

Quantification of microplastic particles often relies on visual sorting from a processed sample and recording the number of particles observed.⁴ For reporting microplastic quantities in the environment, typical units are simply a count of plastic items per unit area or volume, that is, “items per km²” or “items per m³”, although, some previous studies have used mass per mass units as well.^{10,27–29} Pyrolysis-gas chromatography/mass spectrometry (Pyr-GC/MS), Fourier transform infrared spectroscopy (FTIR), focal-plane array (FPA) FTIR, Raman spectroscopy, and scanning electron microscopy (SEM) are qualitative techniques used for identifying and characterizing microplastic polymers.^{4,10,30,31} These techniques are typically used after isolating microplastic particles via a density separation procedure. Density separations are conducted by subjecting environmental samples to concentrated or saturated salt solutions, followed by filtration or other separation techniques, and then optical identification/selection of microplastic particles.^{4,10,12,30,32}

The goals for the present study are to quantify the distribution of microplastic pollution in surface waters of western Lake Superior, to identify polymers present in microplastic debris, and to improve methods for the quantification and identification of microplastics in aquatic environments. Little quantitative data exists for the extent of microplastic pollution in Lake Superior, and no published data exists for far western Lake Superior. Western Lake Superior is a high stress region of the lake^{33,34} impacted by the most populated (110 000 people) and most densely populated urban area (1100 people per square mile) of Lake Superior: Duluth, Minnesota and Superior, Wisconsin (as of the 2016 censuses for the United States and Canada).^{35,36}

In addition, the polymer composition of Lake Superior microplastics has not yet been investigated. In this study, we apply Pyr-GC/MS and ATR-FTIR for qualitative compositional characterization. These two techniques provide different but complementary interrogations of sample composition. Pyr-GC/MS uses pyrolysis to break polymers into smaller moieties, of which the volatile pieces are then separated and identified using GC–MS. In ATR-FTIR the molecular vibrations of polar or transiently polar covalent bonds are measured, through the

change they impart to an evanescent wave penetrating the sample.

Furthermore, previously established methods have been criticized for having a lack of “clean techniques”.³⁷ While a number of investigations of aquatic microplastic pollution have taken place, various publications provide detailed critiques of the commonly used and published methods. These methods have been plagued by variable sample contamination during sampling and processing, difficulty distinguishing among natural materials and microplastics, bias associated with not selecting small and uncolored particles, and inefficient isolation of denser plastics unless heavier and expensive salts like NaI, ZnCl₂, and polytungstates are used in density separations.^{4,25,31,32,37,38} Here, we attempt to address some of these analytical issues. “Clean” analytical techniques are employed, including washing sampling gear methodically between samples, collecting ambient (field) controls, collecting sample processing method blanks, and using lab control samples (LCS) of analytical plastic standards to assess the efficiency of our techniques in isolating microplastics.^{37,39}

MATERIALS AND METHODS

Methodology Motivation and Influence. Methods used here for sampling, sample processing, and analysis were strongly influenced by previous works, in particular NOAA's publication regarding standardized microplastic sampling and sample processing by Masura and colleagues.⁸ Microplastic polymers identified included polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET). These polymers were chosen because they are the most commonly produced and encountered in the environment.^{7,25} These polymers correspond with designator codes 1–6 created by the Society of The Plastics Industry (SPI) and currently used by the American Society for Testing and Materials (ASTM).⁴ While these polymers were the primary references for analysis (see [Supporting Information \(SI\) Table S-1](#) for further details), other polymers isolated, analyzed, and identified were reported as well.

Microplastic particles were defined as belonging to one of six morphological categories (shown in [Figure 1](#), see also [SI, Table S-2](#)), similar to those defined by Crawford and Quinn.⁴ Note that while the effective upper-limit based upon sieving is that at least 2 dimensions were less than 4.0 mm, any nonfibrous particles with a dimension of 4.0–5.0 mm that passed through

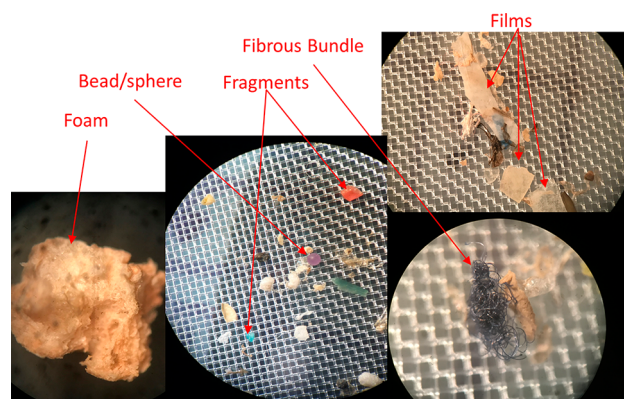


Figure 1. Examples of morphological categories observed during microscopic examinations.

the 4.0 mm sieve, and were captured on the 250 μm sieve, were isolated during microscopy and included in subsequent analyses. Nonfibrous particles determined by microscopy to exceed 5.0 mm in any dimension were not counted as microplastic particles. Despite the use of a 250 μm sieve, the effective minimum size of microplastic particles collected was 333 μm as established by the mesh size of the manta net (see below).

Water Sampling. Twelve sample sites in western Lake Superior were chosen to include key environments speculated to differ in their microplastic distributions based upon proximity to believed sources (local wastewater treatment plant, urban shorelines, and river outflows). These sites were categorized into generalized, regional environments: nearshore, estuary/harbor, and offshore/open water (SI Figure S-1 and Table S-3).

An NQS-45–60 manta tow net (333 μm mesh size, 3 m length, frame opening 14 cm deep by 85 cm wide, Ocean Instruments, San Diego, CA) was used for surface water sampling. At each sample site, a target tow length of 500 to 2000 m was established with length based upon the amount of floating debris. The distance sampled was measured using a Model 2030R flowmeter (General Oceanics Inc., Miami, FL). To avoid sample contamination, the manta net and collection vessel were rinsed thoroughly before each tow. The net was rinsed in surface water without the collection vessel in place, and then was thoroughly rinsed from the outside using an on-vessel lake water hose to prevent sample contamination. Finally, the collection vessel was tripled-rinsed using Millipore water before attaching to the net and beginning a tow.

After a tow was completed, the net was rinsed thoroughly from the outside using the on-vessel hose to concentrate collected materials into the collection vessel. Contents captured in the collection vessel were quantitatively transferred to 4.0 mm and 250 μm metal sieves in series. Materials were hand-shaken on the sieves and washed with Millipore water until it was visually apparent that only collected materials larger than 4.0 mm were present. Contents isolated on each sieve were transferred via forceps and/or water rinses (either Millipore water or <0.7 μm filtered Lake Superior water) into combusted glass containers with Teflon caps. Contents captured on the 4.0 mm sieve that could not be washed through were archived; contents captured on the 250 μm sieve were later subjected to sample processing and analysis. Samples were stored in combusted glass storage vessels in a cool, dark place until they could be further processed in a laboratory.^{9,18}

Due to the potential presence of microplastics in dust around sampling areas,² two clean, empty, and dry Petri-dishes, 5.5 cm in diameter, were placed on the boat while collecting samples. After sampling, the Petri-dishes were rinsed three times with Millipore water and the rinses were collected to establish if ambient plastic contamination had occurred, similar in purpose to the wet filter papers used by Woodall and colleagues.⁴⁰ Petri-dish ambient control samples were later filtered and microscopically examined for microplastic particles. To further prevent sample contamination, cotton or wool based clothes were worn as much as possible during water sampling, sediment sampling, sample processing, and microscopy.

Surface Water Tow and Sediment Sample Processing. To aid in subsequent microscopic examinations, collected materials from sieving were treated to an oxidation step to degrade labile organic matter and a density separation step to isolate lighter plastic particles from denser, primarily inorganic

materials (although some denser plastic polymers may have been included with the inorganic fraction).

For the oxidation procedure, sieved samples were quantitatively transferred to a preweighed beaker, covered with aluminum foil, and dried at 90 °C. After drying, samples were weighed and then subjected to 30% hydrogen peroxide (H_2O_2) treatment catalyzed by Fe^{2+} at 75 °C. The oxidation treatment consisted of adding 20 mL of 30% H_2O_2 (Fisher, Pittsburgh, PA) and 20 mL of 0.05 M ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) to heated sample beakers covered with a watch glass. Once the reaction was visually effervescing, beakers were removed from heat to let the reaction subside. Samples were then again heated for 30 min at 75 °C to ensure that the reaction had been completed. Temperature was monitored by a thermometer present in the sample solution. After these two heating steps, samples were visually assessed for the presence of further organic material. If organic matter persisted, another 20 mL aliquot of 30% H_2O_2 was added with subsequent heating (30 min, 75 °C), and this step was repeated as necessary (typically 3–5 times).⁹

After the oxidation was complete, enough sodium chloride (NaCl) was added to create an approximately 5 M NaCl solution. Contents of the beaker were transferred to covered long stem funnels, where solids denser than the solution (~ 1.15 g/mL) settled overnight. After settling, settled solids were allowed to drain out and archived for later analysis.⁹ The remaining supernatant solution was filtered through 180 μm Nylon filters (Millipore, reference number: NY8H04700, lot numbers: R6BA87287 and R7AA53191). After filtration, sample filters were covered with Petri-dish glass covers in a sealed container with a silica desiccant packet to dry before microscopy. Alternatively, if a more immediate microscopic examination was desired for a given sample, the sample was dried at 90 °C in an oven until moisture content was not visually obvious.

Although the use of NaCl solutions for density separations has been found to be inefficient for separating more dense plastic polymers from environmental matrices,^{4,25,32} NaCl is commonly used in density separations for microplastic particles and has advantages over other salts because it is inexpensive and has less potential for negative environmental impacts.^{4,31,32} The efficacy of using a NaCl solution was evaluated here by analyzing both the supernatant and archived pellets from density separations (SI Table S-7).

Microscopy. Microplastic particles on sample filters were counted and isolated using an Olympus SZH10 microscope. As previous microscopic examinations have been subject to inconsistent particle counts among individual analysts, two analysts conducted microscopic examinations simultaneously. A camera provided a live-feed of the sample to a monitor for both analysts to view during the examination. A custom gridded plastic overlay was taped to the bottom of the Petri-dishes containing the sample filter to help guide analysts through samples efficiently. After examining an individual filter once, the analysts conducted a review scan of the entire filter, including underneath the filter within the Petri-dish to ensure no particles had been missed. Size, color, and morphology of particles were recorded on a spreadsheet before transferring the particles to a preweighed vial, where total microplastic mass was determined prior to qualitative analysis of individual particles. Between collecting individual particles, forceps were cleaned with methanol. Size measurements were made via a micrometer-calibrated ocular scale at 40 \times magnification.

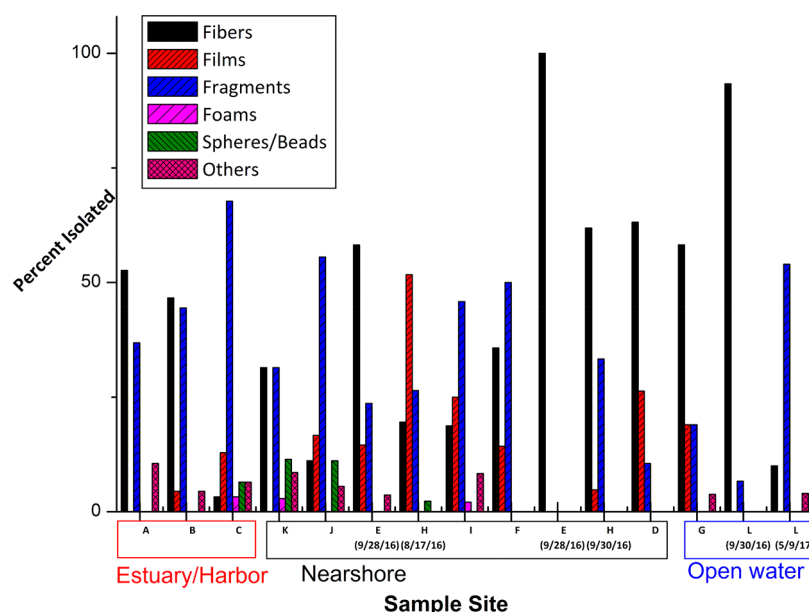


Figure 2. Particle morphology by percent of total particles collected for each surface water site. The frequency of fibers throughout sample sites suggested that atmospheric deposition and greywater/wastewater effluents are significant sources of microplastic particle in Lake Superior. Films and fragments, typically secondary microplastic particles, were likely transported via land runoff, effluents, and riverine inputs.

In order to identify particles as plastic, a “break test” was initially used for the determination of particle composition as plastic or otherwise.⁸ However, this led to the misidentification of many particles, notably cotton fibers, as plastic.⁹ Therefore, a “hot needle” or “melt test” was later adopted for distinguishing among plastic and nonplastic particles.^{41,42} Melt tests were carried out by heating a common sewing needle with a lighter until approximately 2 mm of the needle tip glowed red. The tip was then brought near the particle in question. A “plastic positive” particle liquefied or beaded from melting during this test.⁴¹ The melt test was conducted on analytical plastic standards, polyester fibers, cotton and wool fibers, paint chips from research vessels, and Teflon from a GC vial cap septa to determine its efficacy. All analytical standards and polyester fibers melted in the melt test, cotton and wool fibers burned, and paint chips and Teflon exhibited no noticeable response.

For those samples that predated the melt test, microscopy fiber counts were scaled by the proportion of fibers analyzed by Pyr-GC/MS that indicated plastic polymer composition. These numbers are indicated by asterisks in the relevant tables and figures.

Determination of Polymer Composition (Pyr-GC/MS and ATR-FTIR). Approximately 10% of particles collected in a microscopic examination or a minimum of 5 particles were chosen for analysis from each water sample, with a focus on choosing different morphologies and characteristics, if possible. To establish its mass, each particle was manually inserted into a tared quartz tube, and weighed directly on a Mettler Toledo XP2U microbalance. Before weighing, quartz tubes were cleaned by soaking in NOCHROMIX solution (diammonium peroxodisulfate, Aldrich, St. Louis, MO, USA) overnight, rinsed at least 3 times with Millipore water, and combusted for 4 h at 550 °C.

Pyr-GC/MS analysis used a pyrolysis and thermal desorption unit (TDU) manufactured by Gerstel GmbH & Co. KG, Germany interfaced with an Agilent 7890B Gas Chromatograph and an Agilent 5977A mass-selective detector (MSD). The GC oven was equipped with a 30 m Agilent HP-SMS

column. Particles less than 20 μg were analyzed using splitless introduction into the GC; particles greater than 20 μg were introduced using a 1:100 split. The MSD used electron impact (EI^+ , 70 eV) ionization scanning from m/z 10–550 with the source and quadrupole held at 230 and 150 °C, respectively. See SI Figure SI-3 for further details.

Total ion chromatograms or “pyrograms” of analyzed particles were assessed for polymer identification in three ways. First, the National Institute of Standards and Technology (NIST) mass spectral library (version 2.0, 12/4/12, available through the mass spectrometer’s software package); second, analysis of both plastics standards mentioned previously as well as household products made of known polymers; and third, comparison with published data.^{30,43–45} When pyrograms could not be confidently distinguished as a given polymer due to the low number of pyrolytic products (<3 or 4) and/or low pyrolytic product abundances, pyrograms were evaluated on Mass Hunter qualitative analysis software. Mass Hunter qualitative analysis software was used to integrate total ion chromatogram peak areas of pyrolytic products and calculate a signal-to-noise (S/N) ratio. A 3:1 S/N ratio was used to establish the presence of pyrolytic products, similar to previous studies.^{46–48}

Data from FTIR analysis was obtained to complement Pyr-GC/MS data and further confirm Pyr-GC/MS identifications. A Thermo Nicolet 380 Fourier Transform Infrared Spectrometer using an ATR cell with a germanium (Ge) crystal from SensIR was used for obtaining infrared spectra of isolated microplastic particles. A total of 200 scans were taken and averaged for each spectrum, with a wavenumber resolution of 1 cm^{-1} . All spectra were smoothed by using 11 Savitsky-Golay convolution points⁴⁹ using Origin 8.1, with $\sim 1900\text{ cm}^{-1}$ to 2500 cm^{-1} removed from analysis due to high noise. Particles were chosen for ATR-FTIR analysis if they were easily visible with low risk of difficulty in recovering from the ATR-FTIR unit for subsequent analysis by Pyr-GC/MS. If necessary, particles with the potential to damage the Ge crystal (i.e., irregularly shaped particles like fragments) were ground using a

methanol-cleaned agate pestle and mortar. Between samples, the Ge crystal was cleaned with methanol. Methods summarized by Abdulla and colleagues,⁴ and Crawford and Quinn, as well as comparison to plastic standards listed above, were used for interpreting microplastic particle composition and functional group bands.^{4,49}

QA/QC. Replicate trials of the sample processing protocol were performed using purchased standards from Goodfellow, Inc. and Sigma-Aldrich to assess mass loss and efficiency in isolating microplastic particles. Replicate method blank trials were also performed with 100 mL of Millipore water to further assess contamination during sample processing. For both method blanks and standard analyses, the sample processing protocol was followed as listed above, with the following changes: 3 additions of 10 mL aliquots of 30% H₂O₂ (rather than 20 mL aliquots) were used to accommodate the smaller sample size of test samples. Initial masses of microplastic particles in standards trials for these methods tests ranged from 10 to 21 mg. Results from these tests are given in the SI (QA/QC section).

Statistical Analysis. Microplastic concentrations observed in specific regions (nearshore, offshore, estuarine; see SI Figure S-1) of western Lake Superior were compared to concentrations observed in other regions of the lake as well as the data reported by Eriksen and colleagues for eastern Lake Superior.¹⁸ Variances were evaluated via F-tests among the reported concentrations, analysis of variance (ANOVA) was used to evaluate mean concentrations among study area regions, and a two-tailed *t* test was used to compare mean concentrations. Microsoft Excel 2007's Data Analysis Toolpak was used to conduct statistical analyses. An alpha of 0.05 was used to denote significance for both ANOVA and *t* test analyses.

■ RESULTS AND DISCUSSION

Particle Morphology and Spatial Distributions. 582 microplastic particles were isolated from a total of 1.56×10^{-2} km² of surface water. The most frequent particles observed were fibers (228 particles), followed by fragments (200), and then films (121). Beads/spheres (9), foams (3), and others (21) were observed in lesser quantities (see Figure 2 and SI Table S-2 for morphological definitions).

Fibers, which are typically low mass particles, were the most numerous microplastic morphology in eight of the 15 surface water samples taken in western Lake Superior, including the most offshore site (Site G). Fibers have been shown to be the major component of microplastics delivered by atmospheric deposition.⁵⁰ In addition to atmospheric deposition, riverine²⁶ and wastewater/washer effluents⁵¹ are speculated sources of fibers to surface water sites;²⁶ although atmospheric deposition contributes to these inputs as well⁵⁰ and there is not a clear consensus on the extent to which fibers settle out of these effluents.^{26,50,52} Given the distance of open-lake sampling sites from presumed sources of microplastic particles, it is hypothesized that atmospheric deposition is a significant source of microplastic pollution in Lake Superior (see Figure 2 and SI Figure S-1). Supporting this hypothesis is the low watershed to lake area ratio (~1.55) of Lake Superior,⁵³ which minimizes the impact of riverine inputs. Also supporting this hypothesis are the low human population density in the lake watershed and the large volume of water within the lake (12 230 km³),⁵² which together minimize the impact of wastewater/washer effluent in offshore waters.

The other two dominant morphologies were films and fragments (associated with secondary microplastics)⁴ and shoreline runoff and litter are the most highly suspected sources for these morphologies,² with surface currents likely to bring such particles to offshore locations.¹⁰ For example, Port Wing (site H) is suspected to be impacted by a small local tributary that mobilized plastic and microplastic debris from human-occupied areas.

Particle Abundances in Western Lake Superior and Comparisons to Other Sites. Total surface water microplastic masses in our samples ranged from <0.1 mg to 4.7 mg ± 0.2 mg (uncertainty). Where mass was measurable and normalized to area encompassed, microplastic mass per unit area ranged from 91 to 3538 mg km⁻² (\bar{x} = 1200 mg km⁻²). The largest mass per unit area ratio was observed at the mouth of the Nemadji River (site K, 3538 mg km⁻²), while the smallest measurable mass per unit area was observed at site D (91 mg km⁻²).

To correct for ambient contamination of microplastic particles during sampling and sample processing, the number of particles isolated from each ambient field control (sampling control) and the average number of particles from replicate method blank trials (processing control) were used. Samples were corrected based upon the number of particles isolated from an individual sample's ambient (field) controls and the average particle value in the laboratory method blanks (2.5). A minimum detection limit (MDL) was estimated by using three times the average deviation of the method blanks; thus an MDL of five particles was established. Hence, any samples with fewer than five particles after applying blank correction were deemed under detection limits. In this study only one sample (Duluth Outskirts, Site E, 9/28/16) had a concentration that was under detection limits after correcting.

Areal particle abundances of surface waters (SI Figure S-3) ranged from 0 to 110 000 particles km⁻² (n = 15, \bar{x} : 37 000 particles km⁻² \pm 27 000 particles km⁻²). Estuary/harbor concentrations ranged from 21 000 to 110 000 particles km⁻² (n = 4), open water concentrations ranged from 25 000 to 54 000 particles km⁻² (n = 3), and nearshore concentrations ranged from 0 to 76 000 particles km⁻² (n = 8). On average, the estuary and harbor region had the greatest abundance of microplastic particles (\bar{x} = 54 000 \pm 39 000 particles km⁻²), followed by open water sites (\bar{x} = 38 000 \pm 15 000 particles km⁻²), and then nearshore sites (\bar{x} = 28 000 \pm 21 000 particles km⁻²). The greatest abundance of microplastic particles (110 000 particles km⁻²) was observed at site B (sampled 8/15/16) near the local wastewater treatment plant. The minimum microplastic abundance observed was at site E (sampled 9/28/16) with no detectable particles.

Variances in surface water concentrations among the harbor/estuary, nearshore, and open-water regions (n = 4, 8, and 3, respectively) of the current study were not significantly different (p -value = 0.46). Statistical evaluation of areal microplastic concentrations between the current study (n = 15) and eastern Lake Superior concentrations reported by Eriksen and colleagues (n = 5) did reveal significantly greater variance (p -value = 1.7×10^{-3}) and a significantly greater mean areal microplastic concentration (p -value = 6.4×10^{-4}) in the current study.¹⁸ Land use is likely to be the primary reason for significantly greater concentrations in western Lake Superior; the Twin Ports region is the heaviest anthropogenic stress area of Lake Superior and is more urban than sites investigated by Eriksen and colleagues.^{18,33,34}

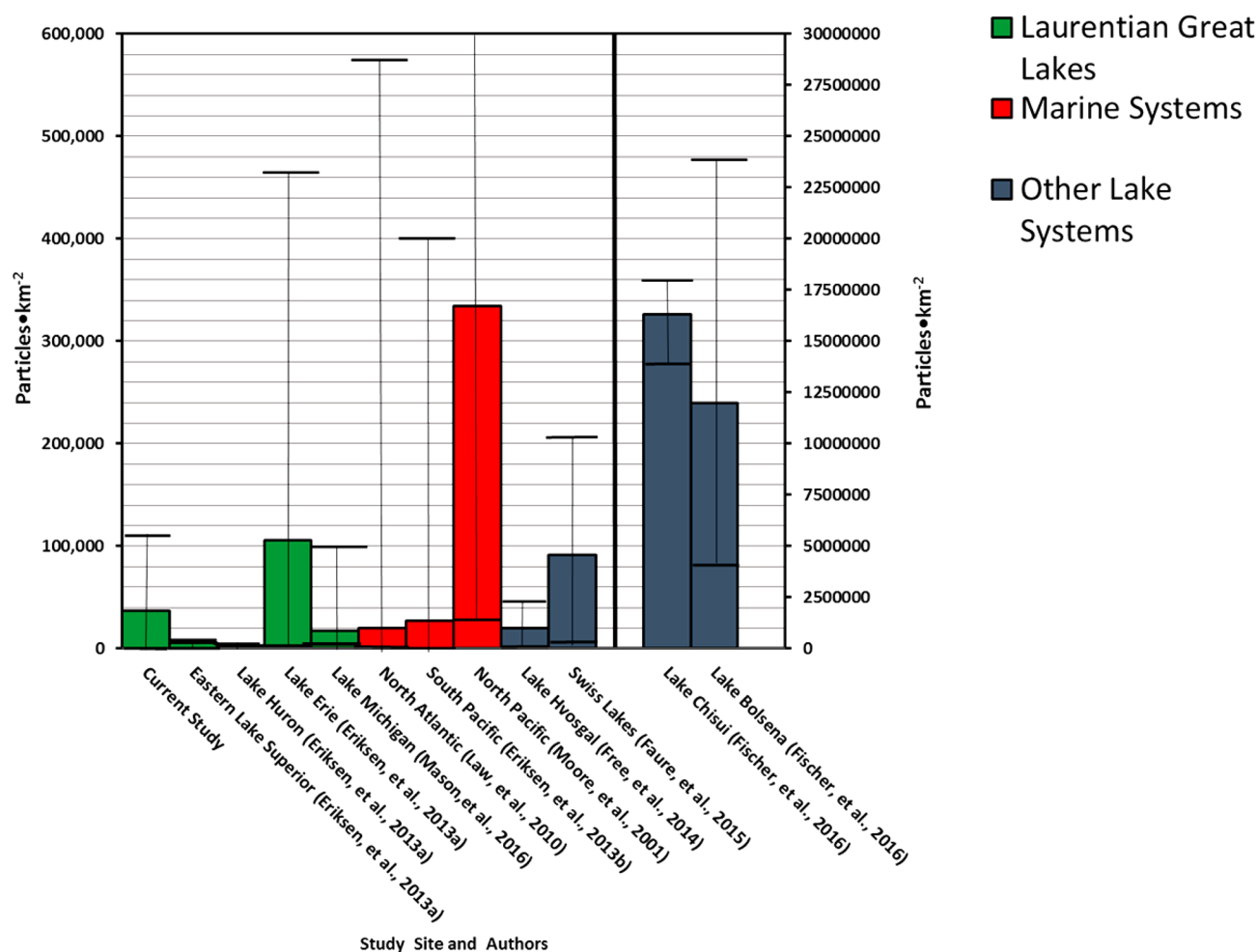


Figure 3. Comparison between the current study, microplastic studies regarding the Laurentian Great Lakes, marine systems, and other inland lake systems. The large bars represent average areal concentrations, and the error bars represent minimum and maximum areal concentrations (all in particles·km⁻²).

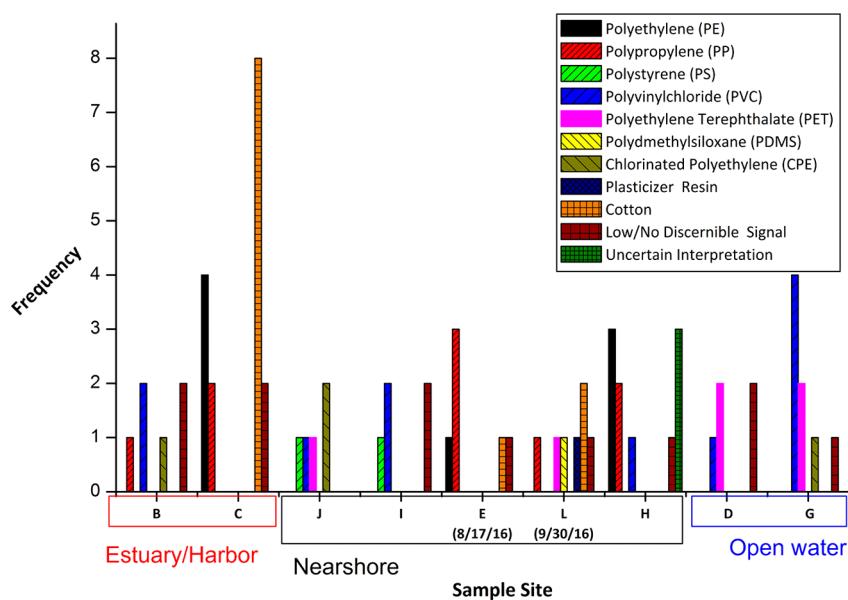


Figure 4. Frequency of particles identified as various polymers at each analyzed surface water site as determined by Pyr-GC/MS. In descending order of most frequently observed plastic polymers: PVC (11), PP (9), PE (8), PET (6), CPE (4), PS (2), PDMS (1), and didecyl phthalate resin (1). Cotton fibers were commonly misidentified in samples prior to the introduction of the melt test (11). Particles with no or low signals (14) were frequently observed; these particles were typically fibers or fragments. In three instances, pyrograms could not be interpreted with certainty.

To assess the magnitude of microplastic pollution in western Lake Superior, concentrations were compared to other investigations of the Laurentian Great Lakes, other inland lake systems, and marine systems (Figure 3). Western Lake Superior microplastic abundances were greater than average values in Lakes Huron (2779 particles km^{-2})¹⁸ and Michigan (17 276 particles km^{-2}),²¹ but lower than average values in heavily urban Lake Erie (105 503 particles km^{-2}).¹⁸ They were similar to values in selected Swiss Lakes (Lakes Geneva-Petit Lac, Zurich, and Brienz; 33,000 particles km^{-2} , 11 000 particles km^{-2} , and 36 000 particles km^{-2} , respectively),¹⁶ and much lower than values found in central Italian lakes Lake Bolsena and Lake Chiusi (1.63×10^7 particles km^{-2} and 1.20×10^7 particles km^{-2}).¹⁵ Its concentrations were comparable to or slightly larger than average values in the north Atlantic Ocean (20 300 particles km^{-2}) and southern Pacific Ocean, 26 898 particles km^{-2}) although the ranges of microplastic abundances in the ocean studies were much larger.^{6,54} For example, northern Pacific Ocean microplastic concentrations reported by Moore and colleagues (\bar{x} : 334 271 particles km^{-2} , range: 31 982–969 777 particles km^{-2})⁵⁵ encompassed but were generally much higher than the average Lake Superior value.

Polymer Identity of Plastic Particles. A total of 68 particles from surface waters were analyzed by Pyr-GC/MS (Figure 4, see also SI Figures S-5–S-29 and Tables S-8–S-15). The most common polymer observed was PVC (11 particles), followed by PP (9), PE (8), and PET (7). Other observed polymers include chlorinated polyethylene (CPE, 4), polystyrene (PS, 2), polydimethylsiloxane (PDMS, 1), and didecyl phthalate plasticizer resin (1). Cotton was commonly analyzed among the particles isolated from dock harbor (site C, 8/15/16) and center bay (site L, 9/30/16), as cotton was frequently misidentified as plastic prior to the introduction of the melt test. Cotton was analyzed in one instance after the introduction of the melt test; this particle was suspected to have entered the sample's GC vial ambiently, rather than through misidentification during microscopy. A total of 14 particles displayed little or no signal and 3 particles could not be confidently assigned single polymer identification.

In total, 19 particles analyzed by Pyr-GC/MS were also analyzed by ATR-FTIR (SI Figures S-21–S-26 and Tables S-15–S-21 for representative spectra). By ATR-FTIR, the most frequently observed polymer was PE (eight, although three of these particles had pyrograms that suggest the particle was not entirely comprised of PE), followed by PET (four, with one pyrogram that suggested the particle was not solely PET), PVC (3), PP (2), and then PS (1) and PDMS (1).

In three instances, the pyrograms of particles resembled PVC or CPE, while the corresponding IR spectrum resembled PE; the speculated cause for this inconsistency between qualitative analysis techniques has been attributed to heterogeneous chlorine content common in the chlorination of PE and PVC.⁵⁶ Similarly, a particle was identified by ATR-FTIR as PET, while the pyrogram had pyrolytic products attributed to cotton and PET. While the particles were identified based on their pyrograms as the primary qualitative analysis technique (due to smaller particle mass required for analysis by Pyr-GC/MS), the inconsistency in polymer identification by different analytical techniques suggests that particles found in the environment may contain copolymers, making the determination of polymer composition difficult.⁴ Given the broad number of possibilities of plastic polymers, copolymers, and additives,^{4,30} in addition to natural processes that can alter

particle composition (including photo-oxidation and biodegradation),⁴ accurate identification of microplastic chemical compositions continues to pose a challenge. Thus, methods should be optimized for distinguishing polymers with greater certainty. For Pyr-GC/MS, pyrograms should yield several pyrolytic products unique to single polymers in appreciable abundances; relying on a single pyrolytic product will not provide sufficient identification. Likewise, IR methods should be optimized to best distinguish between various polymers and the presence of copolymers and additives. While Pyr-GC/MS was chosen here as the primary analytical technique (because it requires little mass while providing in-depth polymer characterization), multiple techniques such as Pyr-GC/MS and FTIR should be used in conjunction with one another to provide high confidence in interpretations.

Most fiber particles analyzed (9) had low/no discernible signals, due to the tendency of fibers to be lower in mass than other particle morphologies. When fibers did yield significant abundances of pyrolytic products, they were primarily identified as PET (seven particles), with lesser instances of PP (2), PVC (1), and uncertain interpretations (1). Fragments were primarily PVC (6), PP (5), or had low/no signals (5); in lower quantities, fragments were identified as PE (1), didecyl phthalate resin (1), or had uncertain interpretations (1). Film particles were found to represent a range of different polymers, including PVC (6), PP (2), PE (6), CPE (4), and PDMS (1). Of the three bead particles analyzed, two were interpreted as PE and PS, while 1 had an uncertain interpretation, but appeared to be PE related. The only foam analyzed was found to be PS (SI Figure S-4).

Fiber particles likely originate mainly from synthetic textile materials due to their frequent identification as PET.¹ The frequency of chlorinated polymers PVC and CPE in a variety of morphological categories reflected the ubiquity of chlorinated polymers. PVC in particular is often used as a structural component, its impact strength making it versatile for a variety of construction applications.^{1,2,53} The common use of PE for food packaging and bags is likely the cause of the prevalence of PE as films.² While PP was found to exist primarily as fragments, due to the diversity in the use of PP (food packaging, car parts, etc.),^{1,2,17} it was difficult to discern the original sources or applications of the particles analyzed. The only foam particle analyzed was likely a secondary microplastic particle of polystyrene foam, a form of expanded PS typically used as packaging.^{1,2}

Microplastics and the Physical Environment. The distribution and fate of microplastic particles in Lake Superior may be subject to certain physical processes more commonly observed in marine environments rather than smaller inland lakes. In Lake Superior, nearshore sites had the lowest concentrations on average, while offshore open-water sites had higher concentrations, similar to microplastic distributions in the western Atlantic ocean as reported by Law et al.⁶ The surface water microplastic abundance at site G (9/30/17) was the third most concentrated of all sites (54 000 particles km^{-2}). Elevated offshore concentrations (like those at the Western Mooring, site G) suggest that microplastic pollution may be mobilized by surface currents and concentrated in convergence zones, similarly to what Law, et al. observed in marine systems⁶ and consistent with mean surface current patterns for Lake Superior.⁵⁷ There may also be greater particle scavenging in nearshore (relative to offshore) Lake Superior, causing quicker transport to the benthos and a reduced concentration in

nearshore surface waters. An additional factor, not yet quantified, is the role of atmospheric deposition of microplastics at various sites in the lake.

Study Implications and Recommendations for Future Work. This study shows that microplastics are a significant component of western Lake Superior's surface waters, with a similar average areal abundance to those seen in the north Atlantic and southern Pacific oceans.^{6,54} The abundance of fibers in Lake Superior prompts speculation as to what the most significant sources of microplastics particles are for this region (atmospheric deposition, effluents, rivers). While some improvements in quantifying microplastic pollution have been introduced here, particularly for using visual microscopy, further research and efforts to standardize and improve methodology across the field are necessary. Future studies need to further optimize methods for assessing microplastic particle contamination during sample collection and processing: they might wish to employ clean-room laboratories to better control for the ambient contamination of microplastic particles, as done for many environmental trace metal and isotopic studies.⁵⁸

Future investigations should also focus on how physical limnological and oceanographic processes affect microplastic particle fate. By further understanding how microplastic particles are delivered and transported and more effectively locating sinks of microplastic pollution, improved sampling regimes and quantitative assessments of microplastic pollution can be obtained. Despite the common perception that polymers denser than water should sink quickly after entering aquatic systems, PVC and PET were both observed in surface water samples, including those from off-shore sites like the Western Mooring (site G) and were isolated from the supernatants of density separation solutions (~1.15 g/mL, see SI).⁹ These observations reinforce the argument that polymer density alone is not the most significant control on microplastic particle fate.^{6,23} Instead, it is likely that microplastic morphology, incorporation into copolymeric materials during manufacturing, and inclusion within aggregates of varying overall densities within an aquatic system may play major roles in determining microplastic distributions within the aquatic environment.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b05829.

Information regarding plastic standards, microplastic morphological definitions, sample site information and maps, maps of microplastic concentrations with corresponding sample sites, particle morphology frequency, polymer frequency, QA/QC results, labeled pyrograms for each polymer identified, mass spectra of selected pyrolytic products, and labeled/interpreted FTIR spectra (PDF)

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■ REFERENCES

- (1) Driedger, A. G. J.; Dürr, H. H.; Mitchell, K.; Van Cappellen, P. Plastic debris in the Laurentian Great Lakes: A review. *J. Great Lakes Res.* **2015**, *41* (1), 9–19.
- (2) Magnusson, K.; Eliasson, K.; Fråne, A.; Haikonen, K.; Hultén, J.; Olshammar, M.; Stadmark, J.; Voisin, A. Swedish sources and pathways for microplastics to the marine environment. A review of existing data. **2016**, No. C 183, 1–87.
- (3) Nerland, I. L.; Halsband, C.; Allan, I.; Thomas, K. V. *Microplastics in Marine Environments: Occurrence, Distribution and Effects*, 2014.
- (4) Crawford, C.; Quinn, B. *Microplastic Pollutants*; Elsevier Inc., 2016.
- (5) Morét-Ferguson, S.; Law, K. L.; Proskurowski, G.; Murphy, E. K.; Peacock, E. E.; Reddy, C. M. The size, mass, and composition of plastic debris in the western North Atlantic Ocean. *Mar. Pollut. Bull.* **2010**, *60* (10), 1873–1878.
- (6) Law, K. L.; Moret-Ferguson, S.; Maximenko, N. A.; Proskurowski, G.; Peacock, E. E.; Hafner, J.; Reddy, C. M. Plastic Accumulation in the North. *Science (Washington, DC, U. S.)* **2010**, *329* (September), 1185–1189.
- (7) Mattsson, K.; Hansson, L.-A.; Cedervall, T. Nano-plastics in the aquatic environment. *Environ. Sci. Process. Impacts* **2015**, *17* (10), 1712–1721.
- (8) Arthur, C.; Baker, J.; Bamford, H. Proceedings of the International Research Workshop on the Occurrence, Effects, and Fate of Microplastic Marine Debris. *Group* **2009**, No. January, 530.
- (9) Masura, J.; Baker, J.; Foster, G.; Arthur, C. Laboratory methods for the analysis of microplastics in the marine environment: Recommendations for quantifying synthetic particles in waters and sediments. *NOAA Technol. Memo. NOS-OR&R-48* **2015**, No. July, 1–29.
- (10) Hidalgo-Ruz, V.; Gutow, L.; Thompson, R. C.; Thiel, M. Microplastics in the marine environment: A review of the methods used for identification and quantification. *Environ. Sci. Technol.* **2012**, *46*, 3060–3075.
- (11) Eerkes-Medrano, D.; Thompson, R. C.; Aldridge, D. C. Microplastics in freshwater systems: A review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. *Water Res.* **2015**, *75*, 63–82.
- (12) Wagner, M.; Scherer, C.; Alvarez-Muñoz, D.; Brennholt, N.; Bourrain, X.; Buchinger, S.; Fries, E.; Grosbois, C.; Klasmeier, J.; Marti, T.; et al. Microplastics in freshwater ecosystems: what we know and what we need to know. *Environ. Sci. Eur.* **2014**, *26* (1), 12.
- (13) Gregory, M. R. Environmental implications of plastic debris in marine settings—entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. *Philos. Trans. R. Soc., B* **2009**, *364* (1526), 2013–2025.
- (14) Imhof, H. K.; Laforsch, C.; Wiesheu, A. C.; Schmid, J.; Anger, P. M.; Niessner, R.; Ivleva, N. P. Pigments and plastic in limnetic ecosystems: A qualitative and quantitative study on microparticles of different size classes. *Water Res.* **2016**, *98*, 64–74.

- (15) Fischer, E. K.; Paglialonga, L.; Czech, E.; Tamminga, M. Microplastic pollution in lakes and lake shoreline sediments - A case study on Lake Bolsena and Lake Chiusi (central Italy). *Environ. Pollut.* **2016**, *213*, 648–657.
- (16) Faure, F.; Demars, C.; Wieser, O.; Kunz, M.; De Alencastro, L. F. Plastic pollution in Swiss surface waters: Nature and concentrations, interaction with pollutants. *Environ. Chem.* **2015**, *12* (5), 582–591.
- (17) Biginagwa, F. J.; Mayoma, B. S.; Shashoua, Y.; Syberg, K.; Khan, F. R. First evidence of microplastics in the African Great Lakes: Recovery from Lake Victoria Nile perch and Nile tilapia. *J. Great Lakes Res.* **2016**, *42* (1), 146–149.
- (18) Eriksen, M.; Mason, S.; Wilson, S.; Box, C.; Zellers, A.; Edwards, W.; Farley, H.; Amato, S. Microplastic pollution in the surface waters of the Laurentian Great Lakes. *Mar. Pollut. Bull.* **2013**, *77*, 177–182.
- (19) Zbyszewski, M.; Corcoran, P. L.; Hockin, A. Comparison of the distribution and degradation of plastic debris along shorelines of the Great Lakes, North America. *J. Great Lakes Res.* **2014**, *40* (2), 288–299.
- (20) Free, C. M.; Jensen, O. P.; Mason, S. A.; Eriksen, M.; Williamson, N. J.; Boldgiv, B. High-levels of microplastic pollution in a large, remote, mountain lake. *Mar. Pollut. Bull.* **2014**, *85* (1), 156–163.
- (21) Mason, S. A.; Kammin, L.; Eriksen, M.; Aleid, G.; Wilson, S.; Box, C.; Williamson, N.; Riley, A. Pelagic plastic pollution within the surface waters of Lake Michigan, USA. *J. Great Lakes Res.* **2016**, *42* (4), 753–759.
- (22) Anderson, P. J.; Warrack, S.; Langen, V.; Challis, J. K.; Hanson, M. L.; Rennie, M. D. Microplastic contamination in Lake Winnipeg, Canada. *Environ. Pollut.* **2017**, *225*, 223–231.
- (23) Corcoran, P. L. Benthic plastic debris in marine and fresh water environments. *Environ. Sci. Process. Impacts* **2015**, *17* (8), 1363–1369.
- (24) Ballent, A.; Corcoran, P. L.; Madden, O.; Helm, P. A.; Longstaffe, F. J. Sources and sinks of microplastics in Canadian Lake Ontario nearshore, tributary and beach sediments. *Mar. Pollut. Bull.* **2016**, *110* (1), 383–395.
- (25) Rocha-Santos, T.; Duarte, A. C. A critical overview of the analytical approaches to the occurrence, the fate and the behavior of microplastics in the environment. *TrAC, Trends Anal. Chem.* **2015**, *65*, 47–53.
- (26) Baldwin, A. K.; Corsi, S. R.; Mason, S. A. Plastic Debris in 29 Great Lakes Tributaries: Relations to Watershed Attributes and Hydrology. *Environ. Sci. Technol.* **2016**, *50* (19), 10377–10385.
- (27) Claessens, M.; Meester, S. De; Landuyt, L. Van; Clerck, K. De; Janssen, C. R. Occurrence and distribution of microplastics in marine sediments along the Belgian coast. *Mar. Pollut. Bull.* **2011**, *62* (10), 2199–2204.
- (28) Ivar do Sul, J. A.; Spengler, Â.; Costa, M. F. Here, there and everywhere. Small plastic fragments and pellets on beaches of Fernando de Noronha (Equatorial Western Atlantic). *Mar. Pollut. Bull.* **2009**, *58* (8), 1236–1238.
- (29) Reddy, M. S.; Shaik, Basha; Adimurthy, S.; Ramachandraiah, G. Description of the small plastics fragments in marine sediments along the Alang-Sosiy ship-breaking yard, India. *Estuarine, Coastal Shelf Sci.* **2006**, *68* (3–4), 656–660.
- (30) Fries, E.; Dekiff, J. H.; Willmeyer, J.; Nuelle, M.-T.; Ebert, M.; Remy, D. Identification of polymer types and additives in marine microplastic particles using pyrolysis-GC/MS and scanning electron microscopy. *Environ. Sci. Process. Impacts* **2013**, *15* (10), 1949.
- (31) Tagg, A. S.; Sapp, M.; Harrison, J. P.; Ojeda, J. J. Identification and Quantification of Microplastics in Wastewater Using Focal Plane Array-Based Reflectance Micro-FT-IR Imaging. *Anal. Chem.* **2015**, *87* (12), 6032–6040.
- (32) Nuelle, M.-T.; Dekiff, J. H.; Remy, D.; Fries, E. A new analytical approach for monitoring microplastics in marine sediments. *Environ. Pollut.* **2014**, *184*, 161–169.
- (33) Sterner, R. W.; Ostrom, P.; Ostrom, N. E.; Klump, J. V.; Steinman, A. D.; Dreelin, E. A.; Zanden, M. J.; Vander, Fisk, A. T. Grand challenges for research in the Laurentian Great Lakes. 2017, No. Eccc 2016.
- (34) Allan, A. J. D.; McIntyre, P. B.; Smith, S. D. P.; Halpern, B. S.; Boyer, G. L. *Joint Analysis of Stressors and Ecosystems Services to Enhance Restoration Effectiveness*, April 2012.
- (35) United States Census Bureau. www.census.gov/newsroom/releases/.
- (36) Statistics Canada. <http://www12.statcan.gc.ca/census-recensement/2016/dp-pd/prof/index.cfm?Lang=E>.
- (37) Twiss, M. R. Standardized methods are required to assess and manage microplastic contamination of the Great Lakes system. *J. Great Lakes Res.* **2016**, *42* (5), 921–925.
- (38) Shaw, D. G.; Day, R. H. Colour- and form-dependent loss of plastic micro-debris from the North Pacific Ocean. *Mar. Pollut. Bull.* **1994**, *28* (1), 39–43.
- (39) Hanvey, J. S.; Lewis, P. J.; Lavers, J. L.; Crosbie, N. D.; Pozo, K.; Clarke, B. O. A review of analytical techniques for quantifying microplastics in sediments. *Anal. Methods* **2017**, *9* (9), 1369–1383.
- (40) Woodall, L. C.; Sanchez-vidal, A.; Paterson, G. L. J.; Coppock, R.; Sleight, V.; Calafat, A.; Rogers, A. D.; Narayanaswamy, B. E.; Thompson, R. C. The deep sea is a major sink for microplastic debris Subject category: Subject Areas: Author for correspondence: 2014.
- (41) Marine & Environmental Research Institute. Guide to Microplastic Identification. 2015; pp 1–15.
- (42) De Witte, B.; Devriese, L.; Bekaert, K.; Hoffman, S.; Vandermeersch, G.; Cooreman, K.; Robbens, J. Quality assessment of the blue mussel (*Mytilus edulis*): Comparison between commercial and wild types. *Mar. Pollut. Bull.* **2014**, *85* (1), 146–155.
- (43) Tsuge, S.; Ohtani, H.; Watanabe, C. *Pyrolysis GCMS Data Book of Synthetic Polymers*; Elsevier: Amsterdam, 2012; p 390.
- (44) Kusch, P. Pyrolysis-Gas Chromatography/Mass Spectrometry of Polymeric Materials. *Adv. Gas Chromatogr. Agric. Biomed. Ind. Appl.* **2012**, *21*.
- (45) Kusch, P. Identification of Synthetic Polymers and Copolymers by Analytical Pyrolysis Gas Chromatography/Mass Spectrometry. *J. Chem. Educ.* **2014**, *91*, 1725–1728.
- (46) Hendrickson, E. S.; Robertson, I. J. An evaluation of illicit stimulants and metabolites in wastewater effluent and the Wisconsin river along the Central Wisconsin river basin. *Acta Sci. Polym. Form. Circumiection* **2015**, *14* (3), 65–74.
- (47) Alvarado, J. S.; Carnahan, J. W. Reductive Pyrolysis for the Determination of Aqueous Sulfur-Compounds With a Helium Microwave-Induced Plasma. *Anal. Chem.* **1993**, *65* (22), 3295–3298.
- (48) Fischer, M.; Scholz-Böttcher, B. M. Simultaneous Trace Identification and Quantification of Common Types of Microplastics in Environmental Samples by Pyrolysis-Gas Chromatography-Mass Spectrometry. *Environ. Sci. Technol.* **2017**, *51* (9), 5052–5060.
- (49) Abdulla, H. A. N.; Minor, E. C.; Dias, R. F.; Hatcher, P. G. Changes in the compound classes of dissolved organic matter along an estuarine transect: A study using FTIR and ¹³C NMR. *Geochim. Cosmochim. Acta* **2010**, *74* (13), 3815–3838.
- (50) Dris, R.; Gasperi, J.; Saad, M.; Mirande, C.; Tassin, B. Synthetic fibers in atmospheric fallout: A source of microplastics in the environment? *Mar. Pollut. Bull.* **2016**, *104* (1–2), 290–293.
- (51) Browne, M. A.; Crump, P.; Niven, S. J.; Teuten, E.; Tonkin, A.; Galloway, T.; Thompson, R. Accumulation of microplastic on shorelines worldwide: Sources and sinks. *Environ. Sci. Technol.* **2011**, *45* (21), 9175–9179.
- (52) Carr, S. A.; Liu, J.; Tesoro, A. G. Transport and fate of microplastic particles in wastewater treatment plants. *Water Res.* **2016**, *91*, 174–182.
- (53) Cotner, J. B.; Biddanda, B. A.; Makino, W.; Stets, E. Organic carbon biogeochemistry of Lake Superior. *Aquat. Ecosyst. Health Manage.* **2004**, *7* (4), 451–464.
- (54) Eriksen, M.; Cummins, A.; Maximenko, N.; Thiel, M.; Lattin, G.; Wilson, S.; Hafner, J.; Zellers, A.; Rifman, S. Plastic Pollution in the South Pacific Subtropical Gyre. *Mar. Pollut. Bull.* **2013**, *68*, 71–76.
- (55) Moore, C. J.; Moore, S. L.; Leecaster, M. K.; Weisberg, S. B. A comparison of plastic and plankton in the North Pacific Central Gyre. *Mar. Pollut. Bull.* **2001**, *42* (12), 1297–1300.

- (56) Huang, J.-C. Miscibility of PVC with chlorinated PE and chlorinated PVC. *Int. J. Polym. Mater.* **2003**, *52* (8), 673–683.
- (57) Beletsky, D.; Saylor, J. H.; Schwab, D. J. Mean circulation in the Great Lakes. *J. Great Lakes Res.* **1999**, *25* (1), 78–93.
- (58) Patterson, C.; Tilton, G.; Inghram, M. Age of the Earth. *Science* **1955**, *121* (January, 21st, 1955), 69–75.